

Thermodynamic study of the galvanizing process in a Zn–0.1%Ni bath

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The addition of alloying elements to the zinc bath is one of the best solution to reduce overthicknesses of the coating when galvanizing silicon-killed steels. The use of nickel addition to the molten zinc offers industrial advantages, especially in the modification of the Sandelin curve related to the reactivity of steels towards the galvanizing bath. However, dross formation in a 0.1 wt % Ni bath is the main drawback of the process.

Bending on thermodynamic description of the ternary Fe–Zn–Ni system at 450 °C, the reaction between a pure iron substrate and a nickel added zinc bath is modelled at 450 °C. The approach of the extension of the liquid phase in the quaternary Fe–Zn–Si–Ni system leads to understanding of the effect of nickel addition to the zinc bath when galvanizing reactive silicon steels. These thermodynamic interpretations lead to understanding of experimental phenomena during the galvanizing process: dross formation, reduction of the coating thickness, smoothing the solid–liquid interface when nickel is added to the zinc bath at 450 °C. Based on morphological and kinetic observations, steel–zinc reactions are clearly investigated showing the important effect of alloying elements to the substrate or to the bath. © 1998 Kluwer Academic Publishers

1. Introduction

Despite the presence of alloying elements in steel, it is frequently observed that during galvanizing at 450 °C, the coating resulting from this reaction nearly obeys the Fe–Zn binary diagram. According to this diagram [1–5], from iron to zinc the following succession of phases is observed: Γ , δ_1 , ζ and η -Zn (Fig. 1). In this case, the kinetics of growth roughly varies as $t^{1/2}$ and thus corresponds to a solid–solid diffusion.

With the introduction of silicon killed and semi-killed steels, the galvanizer was confronted with excessive coating thickness, a grey surface appearance and poor adhesion, when using the normal galvanizing procedures. Fig. 2 shows how the thickness of the zinc coating varies with the silicon content of the steel. Over the range of 0.03–0.12 wt % of silicon, there is a marked increase in the thickness, this being the Sandelin effect [6–11]. When the silicon content exceeds 0.3 wt %, thick coatings are again obtained.

In order to overcome the detrimental effects of silicon on the growth of the zinc–iron intermetallic compounds, several studies were carried out. These research efforts have so far resulted in three solutions which have found their way to in-plant trials and even into industrial practice.

The problem is generally satisfactorily resolved by aluminium additions [12] but its industrial application has been limited because of the rather complicated surface preparation required prior to immersion in the gal-

vanizing bath. Moreover the highly exothermic nature of the Fe–Al intermetallic compounds may leave the Fe–Zn interaction in the presence of aluminium inconsistent and unpredictable owing to the breaking away of layers.

Another solution is based on the high temperature galvanizing process [13] which leads to the elimination of the ζ phase at temperature above 530 °C. However, increased pot and hardware corrosion and excessive dross formation strongly limit the success of this process.

The most recent solution is the zinc–nickel alloy [14–17]. The alloy proved to be convenient for use in galvanizing plants, and it enables galvanizing to be performed successfully on approximately 95% of all steel presented to the galvanizer. When using zinc bath alloyed with nickel ($0.06\% < \text{wt \% Ni} < 0.15\%$), the best effect of nickel additions in the galvanizing baths is to overcome the detrimental effect of silicon in steels. Nevertheless, it builds up in layers which lead to the formation of ternary compounds, and, under some conditions, of floating dross which constitute the main drawback of the process [18].

However, the reactions between the steel substrates, whether containing silicon or not, and the zinc bath alloyed with nickel have not been clearly identified. Thus, the aim of this study is to interpret the experimental phenomena observed, in relation with thermodynamics and kinetics. All arguments will be developed considering supplementary degrees of freedom corresponding

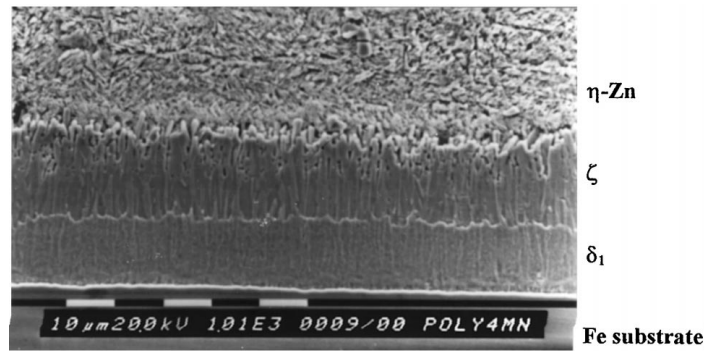


Figure 1 The morphology of the coating when galvanizing a non-reactive (hypo-Sandelin) steel in a pure zinc bath at 450 °C during 5 min.

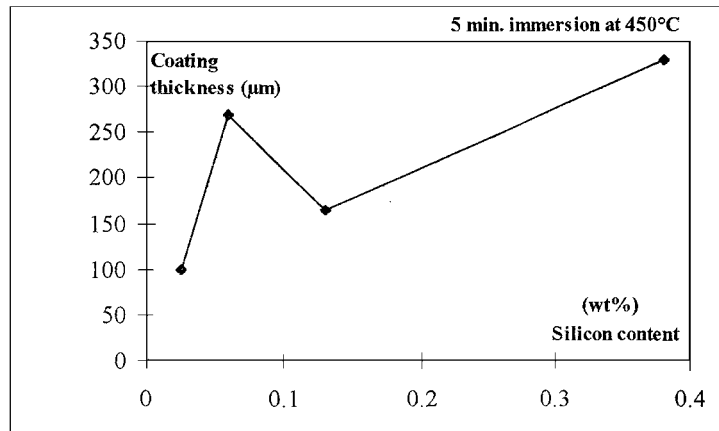


Figure 2 The influence of the silicon composition of steel versus the thickness of the coating when galvanizing industrial steels in a pure zinc bath at 450 °C during 5 min.

to the introduction of an alloying element to the substrate or/and to the bath.

2. Thermodynamics and kinetics backgrounds

The basis of the interpretation of the reactions between silicon-killed steels and the nickel-added zinc bath is the description of the equilibria in the involved ternary diagrams. First the Fe–Zn–Si ternary system was needed to estimate the role of silicon contained in steel on the galvanizing reaction at 450 °C (Fig. 2). Then the influence of nickel additions to the zinc bath when galvanizing iron substrates was shown by the phase equilibria in the Fe–Zn–Ni system at 450 °C.

The Fe–Zn–Si system at 450 °C (Fig. 3) is characterized by the existence of the FeSi compound of which the zinc solubility is about 1 at % Zn and by the low solubility of silicon in the Fe–Zn intermetallic compounds. In fact, electron microprobe analysis shows that the solubility of silicon in the ζ -phase is vanishing and that the δ_1 -phase is likely to dissolve about 1 at % of silicon at 450 °C. This ternary system has been recalculated between 450 °C and 900 °C [19] and confirmed recently [20]. It is worth noticing that the ζ -phase cannot lead to any binary equilibrium with the FeSi compound. Moreover, the excess of silicon in the bath is likely to be reduced in two ways: precipitation of FeSi particles or nucleation and growth of the δ_1 -phase containing silicon.

It is frequently accepted that the first intermetallic compound that appears during the Fe–Zn reaction at

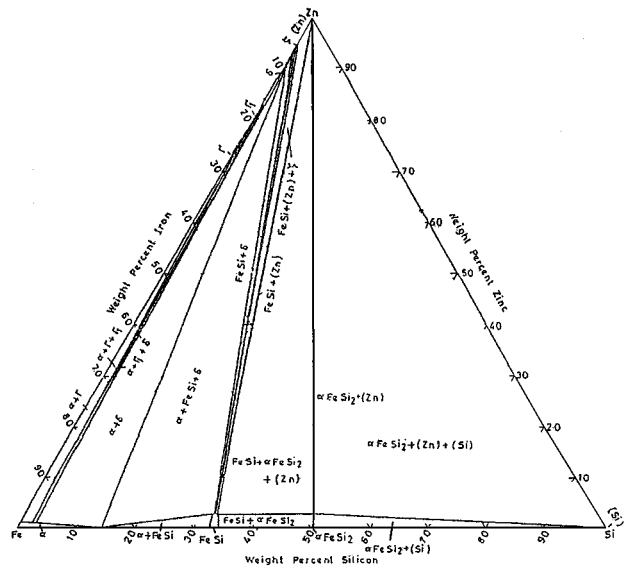


Figure 3 The Fe–Zn–Si ternary system at 450 °C.

450 °C is the ζ -phase. Previous thermodynamic calculations [4] proposed Redlich–Kister parameters for the Gibbs energy of the liquid and α -solid phases in the Fe–Zn system. If the diffusion of zinc in iron is supposed to be negligible at 450 °C, the substrate was shown to be in a metastable equilibrium with the liquid containing about 7 at % Fe. This concentration exactly corresponds to the ζ -compound and thus, during the first immersion time, germination conditions are favourable to the ζ -crystallization near the substrate. Another factor that favours this germination and growth of the ζ -phase

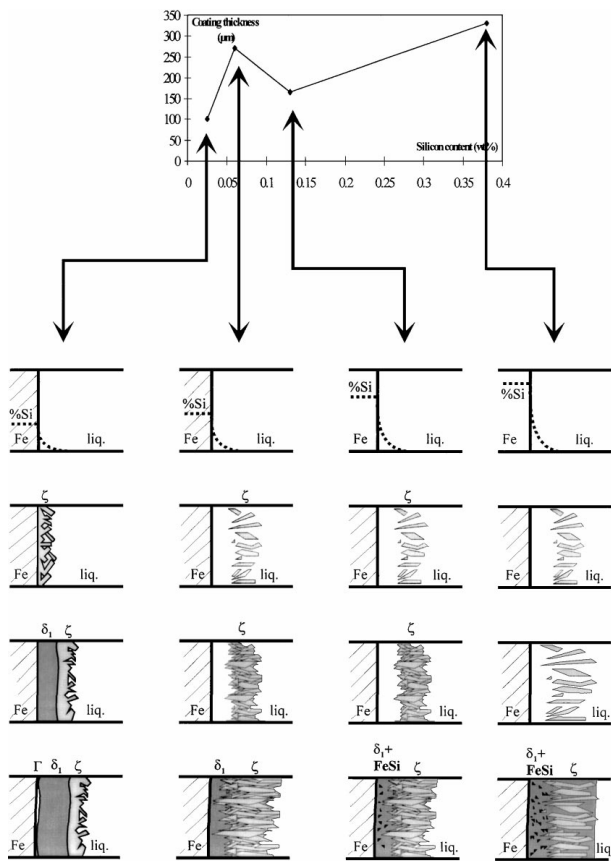


Figure 4 Modelling the steel-zinc reaction when galvanizing silicon killed steels in a pure zinc bath at 450 °C [23].

is related to its crystallographic structure [21] much simpler than that of all other Fe-Zn intermetallic compounds. Galvanizing experiments with short immersion time (< 10 s) also clearly show that whatever the silicon content in the substrate, the coating is essentially formed with the ζ -intermetallic compound [22].

The influence of the silicon content has been proposed in 1993 [23] and is based on previous assumptions and kinetic observations of the growth of the coating (Fig. 4). With the silicon content of the steel, the ζ -crystals may or may not nucleate on the substrate in relation with existence or non-existence of a thin layer of liquid zinc in the vicinity of the steel surface saturated with silicon. So, with Sandelin or hyper-Sandelin steels, the ζ -crystals appear far from the surface of the substrate and then, with the fast iron diffusion in this thin liquid layer, when ζ -crystals are welded together, the silicon supersaturation leads to δ_1 or FeSi precipitation. Overthicknesses are thus observed because kinetics are governed by diffusion to the interfaces. This model was validated by solid-vapour reactions between silicon-killed steels and zinc vapour which do not present this kind of overthickness because of the absence of liquid layer oversaturated with silicon [24].

After previous studies [25, 26], the Fe-Zn-Ni system was definitively [27, 28] characterized by the existence of a continuous series of solid solutions between the Γ_2 -FeZn₄ compound and the Fe₆Ni₅Zn₈₉-dross composition near the zinc-rich corner (Fig. 5). This metastable Γ_2 solid solution, obtained from diffusion experiments, drastically limits the field of the other compounds. Thus, the nickel solubility is 2 at % in the

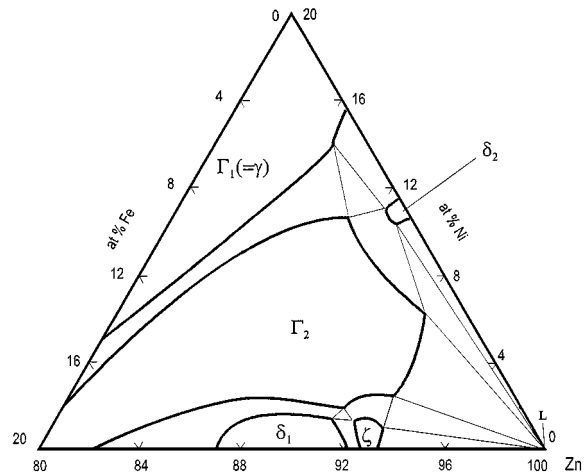


Figure 5 The zinc rich part of the Fe-Zn-Ni ternary system at 450 °C.

δ_1 -FeZn₉ compound and 1 at % in the ζ -FeZn₁₃ compound. Moreover, the δ_2 -NiZn₉ compound dissolves less than 0.5 at % of iron and cannot enter into equilibrium neither with ζ -FeZn₁₃ nor with δ_1 -FeZn₉, because of the extension of the Γ_2 -phase. In any case, liquid at 450 °C can be in equilibrium with one or the other of the ζ -FeZn₁₃ compound, the Γ_2 -solid solution, or the δ_2 -NiZn₉ compound, depending on the Fe and Ni composition in the zinc bath.

Thermodynamic description of the Fe-Zn-Ni liquid [28] is used to explain dross formation in relation with the galvanizing temperature in nickel added zinc bath [18, 29]. Moreover, this formation is directly related to the nickel concentration in the zinc bath and thus to the composition of the liquid in equilibrium with both the ζ and Γ_2 -compounds.

3. Experimental procedure

Four industrial steels of which the silicon content varies from 0.025 wt % to 0.38 wt % have been studied (Table I). These steels are identified as “0” to “3” with increasing silicon content. The non-reactive steel 0 with less than 0.07 wt % Si is a “hypo-Sandelin” steel. Steel 1 with a silicon content near 0.07 wt % can be considered as a “Sandelin” steel. Steels 2 and 3 are characterized as “hyper-Sandelin” steels.

To study the influence of nickel addition to the zinc bath, the galvanizing reactions at 450 °C in a Zn-0.1 wt % Ni bath were compared to those in a pure zinc bath. These two baths were firstly saturated with iron in agreement with the industrial processes.

Before being dipped in the bath, industrial steels were prepared in a classical galvanizing treatment cycle. Steel samples were coarsely polished and then successively cleaned in an alkaline solution, pickled in an

TABLE I Chemical analysis of industrial steels

Steel	Si	C	Mn	P	S	Type
0	0.025	0.05	0.35	0.016	0.005	Non-reactive
1	0.060	0.07	0.86	0.015	0.004	Sandelin
2	0.130	0.14	0.95	0.025	0.001	Hyper-Sandelin
3	0.380	0.14	1.47	0.017	0.005	Hyper-Sandelin

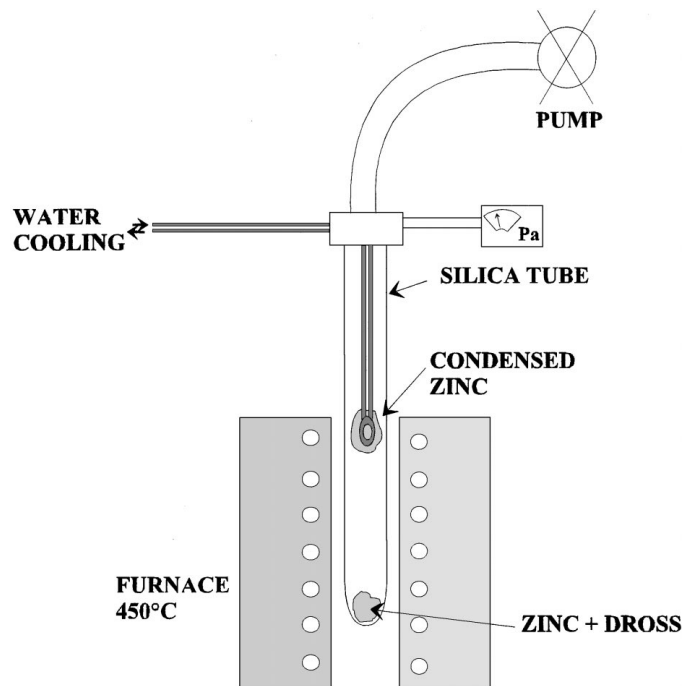


Figure 6 Experimental set-up to separate dross from their zinc environment.

acid solution (HCl + H₂O 50%) to which 2 wt % of a corrosion inhibitor (hexamethylenetetramine) has been added, fluxed in an ammonium chloride and zinc chloride solution and dried at 120 °C. Fluxing enables steel samples to be protected before galvanizing treatment and promotes the attack of the substrate by zinc during the first seconds of reaction. Samples were then dipped at 450 °C for immersion time varying from 3 min to 2 h in one of the two industrial baths. After the galvanizing treatment, they were air cooled. To reveal the galvanizing layers by micrography, samples were cut and polished to 1 μm. Interfaces between the different layers of the coating were shown by chemical pickling in a Nital 4% solution for a few seconds.

Our main means of investigating the coating were optical and scanning electron microscopy coupled with an energy-dispersive spectroscopy system. The thickness of the layers was measured using a micrometer system and crystallographic investigation was performed using a X-ray diffraction goniometer (cobalt anode working with a 40 kV acceleration tension).

After the galvanizing process in each bath, the molten alloyed zinc was solidified. The bottom of the ingot was cut off and polished to study the morphology of the floating dross. To separate these dross from the zinc phase, a technique of zinc evaporation [30] from the ingot was carried out (Fig. 6). The bottom of each ingot and dross obtained after zinc elimination were examined by X-ray diffraction.

4. Results

4.1. Morphological aspects of the galvanizing reaction in a Zn–0.1 wt %Ni bath

When galvanizing at 450 °C for 30 min a non-reactive (hypo-Sandelin) steel in a zinc bath added with 0.1 wt %

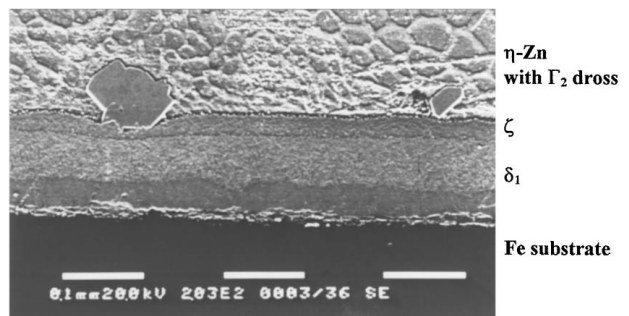


Figure 7 The morphology of the coating when galvanizing a non-reactive (hypo-Sandelin) steel in a Zn–0.1 wt %Ni bath at 450 °C during 30 min.

of nickel (Fig. 7), the layers which constitute the coating display the Γ (1 or 2 μm), δ_1 (20 to 40 μm), ζ (25 to 50 μm) intermetallic compounds and the η -solidified zinc including variable amount of floating dross at the ζ -liquid interface. In comparison with galvanizing in a pure zinc bath (Fig. 1), the nickel addition in the zinc bath leads to smooth the ζ -liquid interface [31]. Moreover, these dross do not appear for immersion times lower than 15 min, which can be considered as the initiation stage of formation of these dross.

When using the zinc evaporation technique on the bottom of the Zn–0.1 wt %Ni ingot, these dross present a polyhedral aspect (Fig. 8) and X-ray diffraction clearly shows they are related to the Γ_2 -compound of which the structure is isotypic with a f.c.c. system with a cell parameter of 1.8 nm (Fig. 9). The main composition of these dross obtained by microanalysis is 89 wt % Zn, 6 at % Fe and 5 at % Ni, well inside the ternary Fe–Zn–Ni system at 450 °C. This composition is related to the stable Γ_2 -dross and it is the reason why it is inside the metastable Γ_2 -domain shown in Fig. 5.

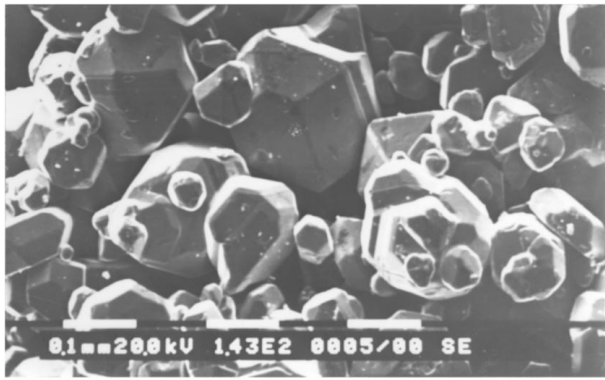


Figure 8 Polyhedral Γ_2 -dross obtained from a Zn-0.1 wt %Ni bath after zinc evaporation.

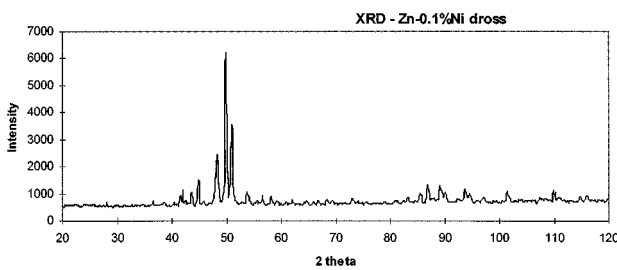


Figure 9 X-ray diffraction pattern of the Γ_2 dross obtained after zinc evaporation.

4.2. Modification of the Sandelin effect with nickel addition to the bath

In order to overcome the detrimental effect of silicon in industrial steels, nickel addition to the zinc bath is one of the best solutions leading to decrease the coating thickness. This well-known effect is confirmed with Fig. 10 which presents a comparison between the influence of silicon on the coating thickness when using a pure zinc bath or a Zn-0.1 wt %Ni bath.

The Sandelin phenomenon is substantially diminished, and the effect of nickel addition is clearly visible with reactive “Sandelin” steel containing about 0.07 wt % of silicon. Galvanizing non-reactive steels

leads to thinner thicknesses which may be a drawback of the process in reference with the corrosion behaviour depending on the thickness of the coating. With silicon killed steels (reactive “hyper-Sandelin” steels), the over-thicknesses of the coating are not modified by the addition of nickel into the zinc bath.

In industrial practice, it is thus clear that with the introduction of a supplementary element such as nickel the thicknesses of the layers are rather less developed than expected from conventional galvanizing bath. A direct consequence is the increasing of the “galvanizable” steels categories in relation with their silicon content.

4.3. Kinetics of growth of the coating

Constituting the coating, each layer has its own kinetics of growth. Fig. 11 shows the most part of the growth being the fact of the δ_1 -layer. Its kinetics is linear with the square root of the immersion time, which corresponds to a solid–solid diffusion. In this case, iron and zinc atoms diffuse according to the classic Fick’s law.

The growth of the ζ -layer is more complex and is clearly inhibited by the presence of nickel into the bath. After a growth mechanism controlled by diffusion, from a immersion time neighbouring 15 min, the ζ -layer does not increase any more and its thickness is kept constant (about 25 μm). This time for which the growth regime changes clearly corresponds to the formation of the Γ_2 -dross at the ζ -liquid interface.

4.4. Long immersion time in a Zn-0.1 wt %Ni bath

In order to define the behavior of the Γ_2 -dross at the ζ -liquid interface with the immersion time, long time galvanizing (48 h) of a non-reactive steel was envisaged in a Zn-0.1 wt %Ni bath at 450 °C. Fig. 12 shows the succession of the Γ , δ_1 and ζ -layers already observed, but with long immersion times a continuous layer between the ζ -compound and the η -solidified zinc is visible. This compact layer is clearly constituted by welded

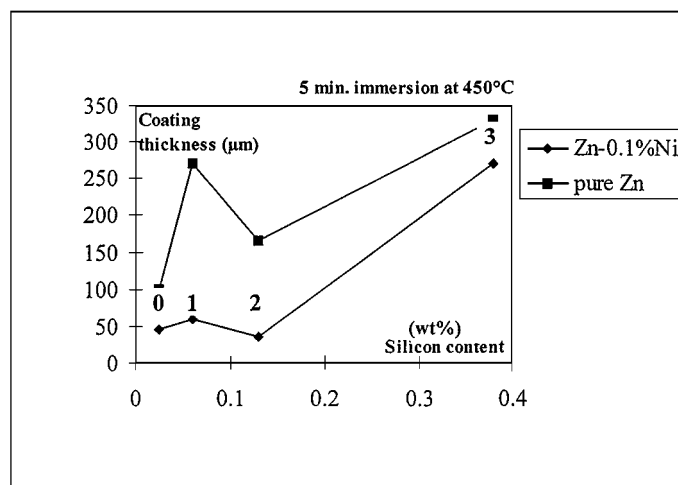


Figure 10 The influence of the silicon composition of the steel when galvanizing industrial steels in a pure zinc bath and a nickel-added zinc bath and at 450 °C during 5 min.

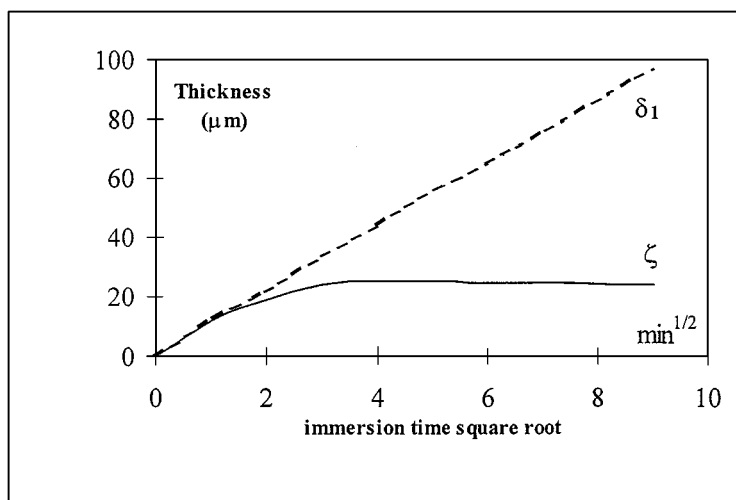


Figure 11 Kinetics of growth of the δ_1 and ζ layers when galvanizing a non-reactive (hypo-Sandelin) steel in a Zn-0.1 wt%Ni at 450 °C.

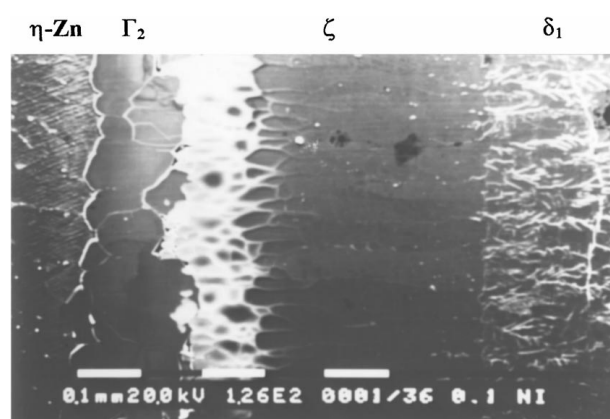


Figure 12 The morphology of the coating when galvanizing a non-reactive (hypo-Sandelin) steel in a Zn-0.1 wt%Ni bath at 450 °C during 48 h.

Γ_2 -dross, which modifies the equilibria between phases in the Fe-Zn system by introduction of nickel.

Kinetics of growth of the different layers agree with the linear dependance with time square root of the δ_1 -thickness and the non-evolutive ζ -layer (about 25 μm). The ζ -liquid interface observed with short immersion time is replaced by a smooth ζ - Γ_2 interface. The Γ -layer between the substrate and the δ_1 -compound is always thin, even with 48 h treatment.

In fact, a diffusion path from the iron substrate to the zinc bath containing 0.1 wt% of nickel and saturated with iron is successively crossing the Γ , δ_1 , ζ , and Γ_2 -domains in the ternary Fe-Zn-Ni diagram at 450 °C. This Γ_2 -layer impedes the evolution of the ζ -layer with the immersion time which is kept constant.

5. Discussion

With reference with the model [23] of growth of the coating when galvanizing reactive or non-reactive steels, confirmed by recent studies [32], the nickel additions to the zinc bath considerably change kinetics, morphologies and thermodynamic equilibria between Fe-Zn phases. In order to define the role of these additions, previous experimental results were confronted

with thermodynamic evaluations of diagrams to lead to the best comprehension of the industrial process.

In a first interpretation considering the ternary Fe-Zn-Ni at 450 °C, the proposed model explains different results obtained when galvanizing pure iron substrates in a nickel-added zinc bath. Then, using equilibria between the liquid phase and other intermetallic compounds in the Fe-Zn-Ni-Si quaternary system at 450 °C, an interpretation is proposed about the reduction of the “Sandelin” effect with nickel addition to the zinc bath.

5.1. The galvanizing process of pure iron in a Zn-0.1 wt%Ni bath

When galvanizing iron substrates at 450 °C in a zinc bath containing 0.1 wt% of nickel, the main experimental differences with a conventional galvanizing in a pure zinc bath are:

- the Γ_2 dross formation from immersion times exceeding 15 min
- the smoothing of the ζ -liquid interface
- the existence of a compact and continuous Γ_2 layer with long immersion times.

The reaction between the iron substrate and the Zn-0.1 wt%Ni bath at 450 °C is modelled in Fig. 13. A schematical aspect of the zinc rich corner of the Fe-Zn-Ni system is proposed showing the ζ , Γ_2 and liquid phases and the different equilibria between themselves. This model is relying on the metastable equilibria between phases in terms of the immersion time of the galvanizing reaction.

In this Fig. 13, at time t_i , the composition of the liquid phase is represented as l_i , the composition of the ζ -phase in equilibrium with this liquid is labelled z_i and the Γ_2 dross composition which is equivalent as $\text{Fe}_6\text{Ni}_5\text{Zn}_{89}$ is shown as point g . Like each composition l_i of the liquid phase, the mean composition l of the zinc bath is on the liquidus curve of the ternary Fe-Zn-Ni diagram, because the bath containing 0.1 wt% of nickel is supposed to be saturated with iron [28].

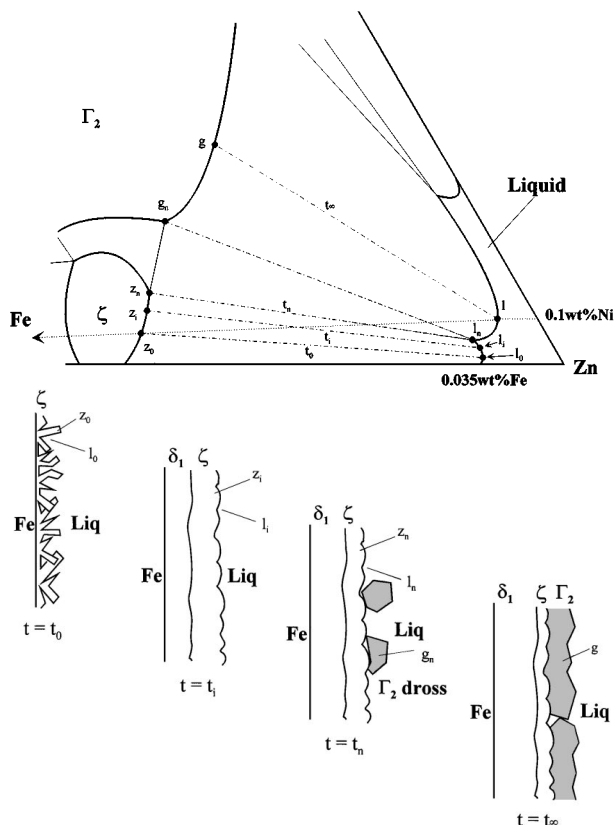


Figure 13 Modelling the galvanizing reaction of a pure iron substrate in a Zn-0.1 wt %Ni bath at 450 °C.

During the first time of immersion, at time t_0 , the iron substrate is dipped in the zinc bath, and thus the couple of diffusion is characterized by the Fe point and the l composition of the bath. The virtual line linking these two points is crossing all the Fe-Zn intermetallic compounds containing various amounts of nickel. According to thermodynamic [4], structural [21] and kinetic [22] considerations, the ζ -compound is heterogeneously nucleated on the iron substrate. Thus, at time t_0 , the composition of the ζ -compound is given as z_0 and the tie-line in the biphased ζ -liquid domain indicates the composition of the liquid phase as l_0 . The schematic aspect of the nucleation of the ζ -compound shows the morphology of this thin layer formed by small dendrites of the ζ -phase. These crystals are analogous to the crystallographic structure of ζ and the metastable composition l_0 of the liquid phase surrounding these dendrites.

When the immersion time t_i increases, in relation with interdiffusion of iron and zinc atoms between the substrate and the ζ -layer already formed, the δ_1 -layer appears. Moreover, as the mean composition of the bath is kept constant as l , the composition of the liquid phase neighbouring the ζ -layer evolves on the liquidus curve towards richer amount of nickel. At time t_i , the composition of the liquid phase is l_i and thus, the tie-line gives the composition of the ζ -layer in equilibrium with the molten zinc as z_i . According to nickel diffusion from the bath into the coating, the composition of nickel in the intermetallic compounds increases especially in the ζ -phase as shown in the Fe-Zn-Ni diagram. In this case, previous ζ -crystals are continuously in a zinc bath of which the nickel composition is increasing. Like dissolution of a piece of sugar in pure coffee, metastable

equilibria promotes erosion of the crystals and thus the ζ -liquid interface is smoothed with immersion time.

When the equilibria between phases are progressed to stability, at time t_n , the compositions of the liquid phase and the ζ -compound respectively reach l_n and z_n . In this situation, the composition of the liquid phase is such as the liquid enters in equilibrium with both the ζ and Γ_2 -phases. Conditions of germination of the Γ_2 dross are thus favourable just at the ζ -liquid interface where the liquid phase composition is l_n . So, at time t_n , experimentally estimated to 15 min, dross may be observed and their main composition is related to g_n . In this case, all the amount of diffused iron from the coating to the bath exclusively serves to the growth of these Γ_2 dross and thus the thickness of the ζ -layer do not evaluate for immersion time exceeding 15 min. However, the δ_1 -layer linearly increases with the square root of immersion time according to a solid-solid diffusion of atoms.

For a long time of immersion t_∞ , when equilibria are supposed to be reached, whatever is the location, the liquid phase composition is l and thus, the tie-line bending from this composition to the Γ_2 domain indicates the dross composition as g . In this case, the growth of the dross is such as a compact and continuous layer of Γ_2 is formed prohibiting any equilibrium between the liquid phase and the classic Fe-Zn intermetallic compounds. The composition of this Γ_2 layer is g , and a diffusion path from the substrate to the liquid phase is successively crossing the Γ , δ_1 , ζ and Γ_2 domains. In fact, it has been experimentally verified that the g composition of the Γ_2 -Fe₆Ni₅Zn₃₉ stable dross obtained after zinc evaporation is quite different than that of the metastable Γ_2 -dross neighbouring the ζ -liquid interface of the coating of which the composition is defined as g_n .

For an infinite time of immersion, when the iron substrate is dissolved, if the amount of the liquid phase is supposed to be large enough, thermodynamic equilibria in the Fe-Zn-Ni system at 450 °C lead to a Γ_2 -liquid equilibrium. So, we can suppose that every intermetallic compounds (δ_1 and ζ) are dissolved and essentially Γ_2 dross are present. This interpretation is easily confirmed by the industrial presence of a large amount of dross in the bottom of ceramic crucible of zinc added with nickel.

5.2. The galvanizing process of silicon killed steels in a Zn-0.1 wt %Ni bath

Experimental results shown in Fig. 10 clearly indicate the evident effect of nickel addition to the zinc bath on the galvanizing reaction between silicon killed steels and the molten bath at 450 °C. An interpretation of the phenomena is based on the description of the phases equilibria in the quaternary Fe-Zn-Ni-Si system at 450 °C, especially in the zinc rich corner of the diagram according to the important role of the liquid phase. This system has not been yet established and thus equilibria between phases are still quite unknown. Fig. 14 shows a schematical aspect of the liquid domain at 450 °C and the liquidus surface indicates

TABLE II Chemical composition of the biphased and triphased points on the liquidus surface of the quaternary Fe–Zn–Ni–Si system at 450 °C

Points	at % Fe	at % Ni	at % Si	Equilibrium	Reference
<i>a</i>	0.038	0	0	Liq– ζ	[1–5]
<i>b</i>	≈ 0.038	0.06	0	Liq– ζ – Γ_2	[18, 25–28]
<i>c</i>	≈ 0.038	0	< 0.001	Liq– ζ – δ_1	[19, 20]
<i>d</i>	≈ 0.0035	≈ 0.6	0	Liq– δ_2 – Γ_2	[28]
<i>e</i>	0	0.6	0	Liq– δ_2	[25–28]
<i>f</i>	≈ 0.038	0	< 0.001	Liq– δ_1 –FeSi	[19, 20]

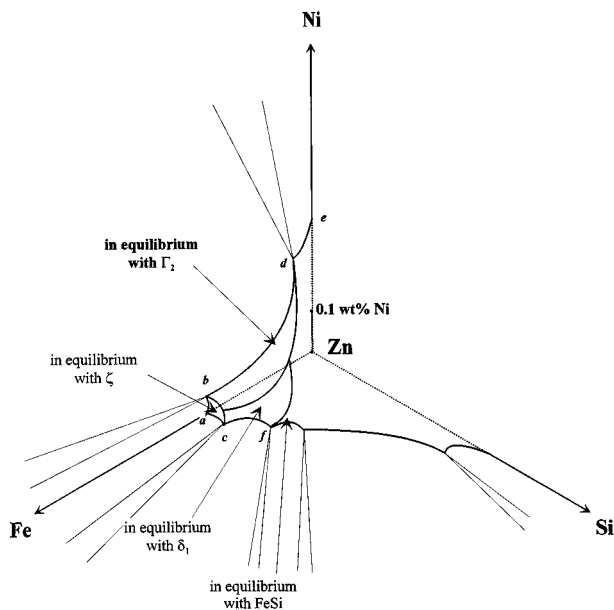


Figure 14 The schematic aspect of the liquidus surface in the quaternary Fe–Zn–Si–Ni system at 450 °C (the composition of points *a* to *f* is given in Table II).

multiple equilibria between solid phases and liquid. In this representation, orthogonal axis are chosen to simplify reading and already known equilibria are presented. Table II gives the main compositions of the biphased and triphased points of the liquidus surface whereas it is not totally described.

The interpretation relative to the effect of nickel addition, emphasized by the modification in the Sandelin curve (Fig. 10), is based on the acceptance of the model of the galvanizing reaction of silicon-killed steels [23]. The main conclusion of this model is the existence of a silicon rich liquid layer neighbouring the steel substrate which impedes the heterogeneous formation of the ζ -crystals on this substrate. The thermodynamic traduction of this interpretation is given by equilibria between the liquid phase and the δ_1 or FeSi compounds when silicon is introduced in the galvanizing reaction. In this case, stable equilibria between this liquid phase and the ζ -compound is prohibited.

If nickel is added to the molten bath, and if we suppose the galvanizing coating on silicon killed steel is become to a “hypo-Sandelin” type with such addition, it means that nickel favours the formation of ζ -crystals on the substrate like in the case of the galvanizing of hypo-Sandelin steels in a pure zinc bath. A consequence is that with nickel addition the enriched liquid layer with silicon does not exist, or in other words, the equilibrium

between the liquid phase and the ζ -compound is kept whatever is the silicon content in the steel substrate. However, in relation with the description of the ternary Fe–Zn–Ni system at 450 °C [28], 0.1 wt % of nickel added to the molten bath promotes the equilibrium between the liquid phase and the Γ_2 -compound. This important value shows that a steel substrate may not lead to any equilibrium between the liquid phase and the ζ -compound which is inconsistent with previous hypothesis: the galvanizing coating obtained with a reactive steel may never be related to a “hypo-Sandelin” type but the thickness of the coating is just reduced in comparison with that obtained in the galvanizing reaction of a Sandelin steel. The main consequence is that the influence of nickel addition to the zinc bath is not effective in relation with the ζ -germination. On the other hand, its effect is evident with the growth of the ζ -crystals. In fact, the metastability of these ζ -crystals in the liquid phase containing 0.1 wt % of nickel is such that their growth is clearly limited by their already mentioned erosion by the nickel enriched liquid phase. This interpretation may be confirmed by the thickness of the coating obtained by reaction of non-reactive steels in a zinc bath containing nickel : few modification is noted in relation with the nickel effect (Fig. 10).

5.3. Modelling the reaction between a Fe–Si substrate and a Zn–Ni bath

In relation with the model of the galvanizing reaction of silicon-killed steels in a pure zinc bath [23], four kinds of steels are considered in our interpretation and are labelled “0” to “3” according to Table I. Equilibria between the liquid phase and intermetallic compounds are used in the quaternary Fe–Zn–Si–Ni system at 450 °C.

In our model (Fig. 15), for steels *i* (*i* = 0 to 3), L_i is the silicon composition of the liquid phase at the substrate-liquid interface when dipping steel *i* in a pure zinc bath saturated with iron. When adding 0.1 wt % of nickel to the molten bath, the composition of this liquid layer neighbouring the substrate increases from L_i to L'_i . This point L'_i is generally situated in a biphased domain and thus a tie-line bending the liquid phase to a solid intermetallic domain crosses L'_i . Point L''_i is defined by the intersection of this tie-line with the liquidus surface of the quaternary system.

Considering the previous model [23], when galvanizing non-reactive steel “0”, the composition L_0 is so small and lower than point *c* that the equilibrium between the liquid phase and the ζ -compound is kept. In this case, nickel addition modifies the composition from L_0 to L'_0 and the situation is not so different than that obtained with a pure iron substrate. The point L'_0 is thus in the biphased Γ_2 -liquid domain and the point L''_0 is onto the portion of the liquidus surface representing a Γ_2 -liquid equilibrium. The galvanizing process is quite the same that the one exposed in Fig. 13. In this case, thinner thicknesses of the coating are obtained and Γ_2 dross are present at the ζ -liquid interface.

When galvanizing a “Sandelin” steel labelled “1”, the L_1 composition of the liquid layer neighbouring the substrate is now upper that point *c* but lower that

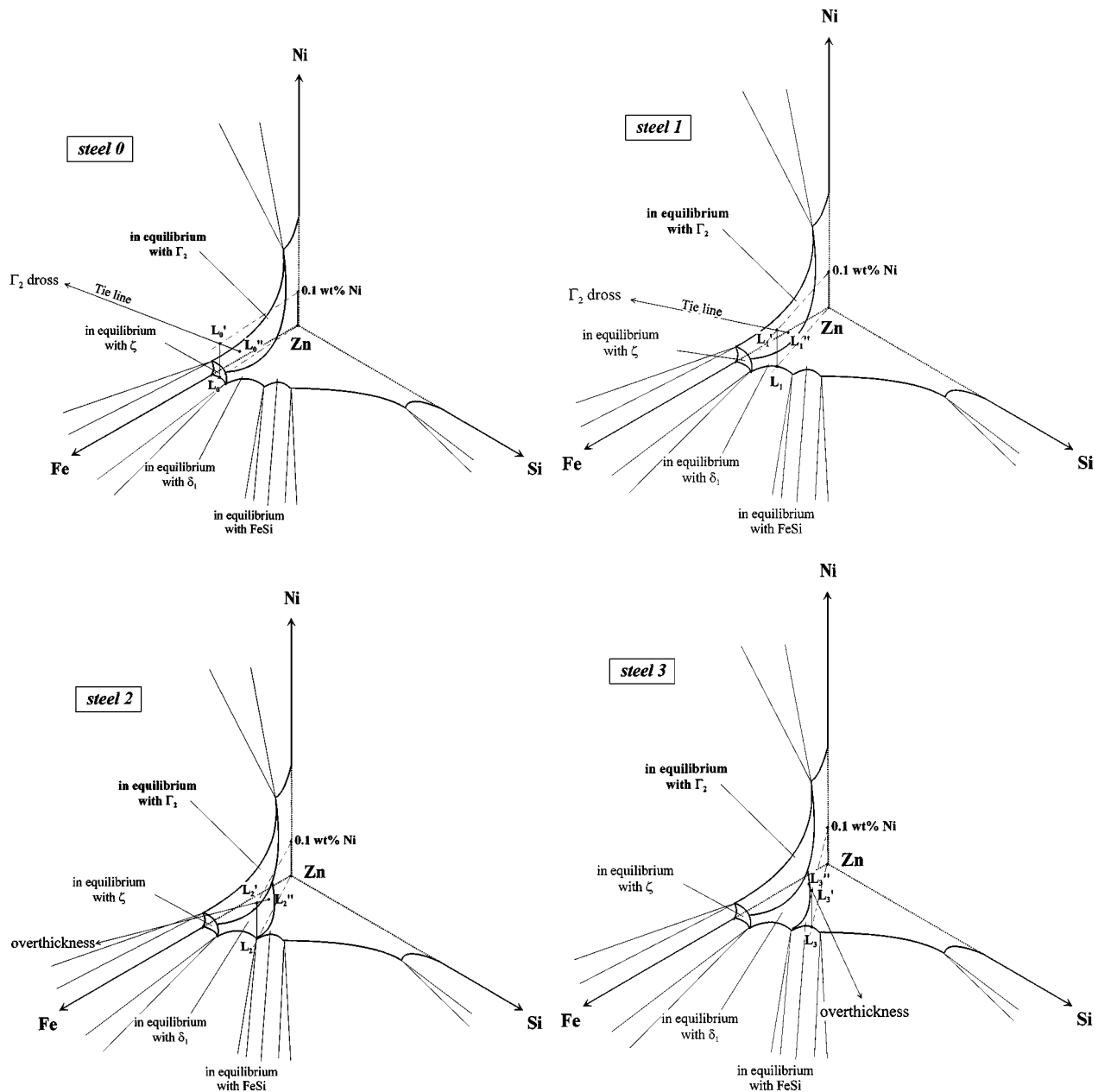


Figure 15 Modelling the galvanizing reaction of silicon killed steels in a Zn–0.1 wt % Ni bath at 450 °C (The compositions of steels 0 to 3 is presented in Table I).

point *f*. The ζ -liquid equilibrium is thus replaced by a δ_1 -liquid equilibrium which lead to impede the heterogeneous formation of the ζ -crystals. However, when adding 0.1 wt % of nickel to the molten bath, point L'_1 is kept in the biphased Γ_2 -liquid domain because the silicon solubility in phase is very low. Like in the previous case, point L''_1 is onto the surface of the liquidus in equilibrium with the Γ_2 compound and phenomena are not so different that in the case of galvanizing non-reactive steels. The nickel addition smoothes the ζ -liquid interface and decreases the thickness of the coating which is thinner than those obtained with “Sandelin” substrates in a classical galvanizing bath. Γ_2 dross may be observed in relation with the tie-line bending L'_1 to L''_1 .

The situation is completely modified when galvanizing steel “2” because the L_2 composition reaches point *f*. By nickel addition, point L'_2 moves in a biphased δ_1 -liquid domain and thus point L''_2 represents a liquid phase in equilibrium with the δ_1 compound. Dross

composition may be different and nickel effect is no more evident. Overthicknesses may be obtained with such steels if the silicon composition is not well controlled. Nevertheless the silicon effect is attenuated by nickel addition smoothing the solid-liquid interface.

With “hyper-Sandelin” steel “3”, the galvanizing phenomena leading to overthickness are increased by the effect of high silicon content in steel. Point L_3 (larger than point *f*) is related to an oversaturation in silicon which promotes the equilibrium between the liquid phase and the FeSi compound. When adding nickel to the zinc bath, the composition L'_3 is referred to a possible equilibrium between the liquid phase, the δ_1 and/or the FeSi compounds. In such a case, the L''_3 liquid phase may be in equilibrium with both the δ_1 and FeSi compounds, and thus the silicon activity is so important in the steel substrate that whatever is the nickel content in the bath, overthicknesses are always present. Moreover, kinetics of growth of the coating is not modified by the

addition of nickel and thicknesses are quite similar than that obtained with the use of a pure zinc bath.

6. Conclusions

The understanding of the effect of nickel addition to the molten zinc when galvanizing silicon killed steels is based on the interpretation of the conjugated role of silicon in the iron substrates and nickel in the bath. Modelling these reactions leads to understand experimental phenomena such as the modification of the aspect of the ζ -liquid interface, the formation of dross, and the modification of the Sandelin curve by addition of nickel to the galvanizing bath.

Considering thermodynamic descriptions of the ternary Fe–Zn–Ni system at 450 °C, our model shows the important role of kinetics and especially the evolution of morphologies as a function of the immersion time. Modifications during the galvanizing treatment may occur, leading to dross formation or metastable equilibria between phases. Moreover, our interpretation is confirmed by experimental results concerning the influence of the temperature treatment on the formation of the galvanizing coating [28].

Approaching the equilibria in the quaternary Fe–Zn–Si–Ni system at 450 °C, the main difference between the use of a classic zinc bath or a alloyed nickel bath are understood and the reduction of the Sandelin phenomenon is interpreted. The effect of nickel addition is essentially shown by the modification in the growth of the ζ -crystals which enter in a metastable equilibrium with liquid. The equilibria between the Fe–Zn intermetallic compounds and the liquid phase are shift to the Γ_2 -liquid equilibrium when galvanizing steels of which the silicon content is less than 0.1 wt %. On the other hand, when reactive steels are treated, the silicon activity is so important that 0.1 wt % of nickel added is too weak to modify the reactivity of these substrates.

The poor knowledge of the equilibria in the quaternary Fe–Zn–Ni–Si system does not allow to estimate the existence of binary Ni–Si or ternary Fe–Ni–Si compounds containing various amount of zinc. Nevertheless, affinities between nickel and silicon [33] may lead to these precipitations which could compromise any equilibrium between the liquid phase and the FeSi compound. In this case, thermodynamic stability of these compounds in presence of molten zinc would also lead to the reduction of the “Sandelin” phenomenon.

In correlation with this study, one of the best solutions to modify the reactivity of steels in the zinc bath would be to add a supplementary degree of freedom [34] in the equilibria between phases. Alloying bath with transition metals is the usual method to reduce the Sandelin phenomenon. With the same idea, aluminium [35, 36], manganese [37], titanium [38, 39] or tin [40] have already been studied and our models concerning the nickel influence may directly be transposed to these metals.

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